

Nd(III)/Am(III) Interactions with Borate in NaCl Solutions: Speciation and Solubility as a Function of pH_m

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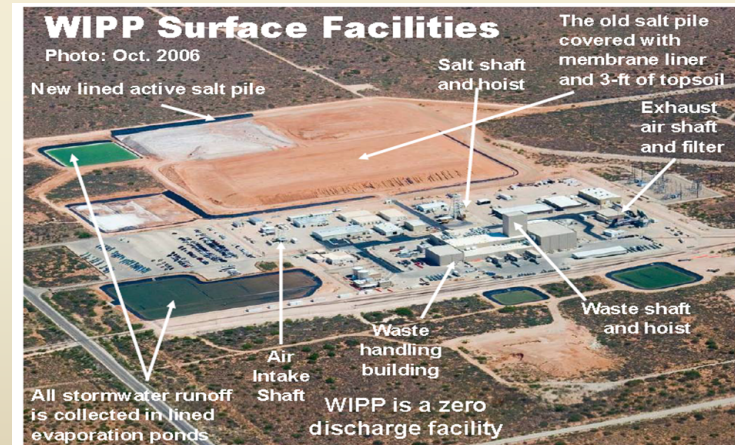


OUTLINE OF PRESENTATION

- Introduction
- Objective of This Work
- WIPP Borate Speciation Scheme
- Speciation of Am(III) in NaCl Solutions in the presence of Borate as A Function of pH_m
- Solubility of Am(III) in NaCl Solutions in the presence of Borate as A Function of pH_m
- Summary

INTRODUCTION

- The accurate knowledge of actinide solubilities that could be dissolved in natural brines is important to safe disposal of nuclear waste.
- Recent experimental work indicates that borate could form an aqueous complex with rare earth elements such as Nd(III) and Eu(III) at 25°C (Borkowski et al. 2010; Schott et al., 2014, 2015), analogs to Am(III).
- Borate is a species with significantly high concentrations in natural brines:
 - The borate concentrations in the Waste Isolation Pilot Plant (WIPP) brines
 - Generic Weep Brine (GWB): $0.180 \text{ mol} \cdot \text{kg}^{-1}$ and
 - U.S. Energy Research and Development Administration Well 6 (ERDA-6): $0.0692 \text{ mol} \cdot \text{kg}^{-1}$ (Xiong and Lord, 2008)
- Therefore, the assessment of contributions of borate complexation to solubility of Am(III) is needed.



Borkowski, M., Richmann, M., Reed, D.T., and Xiong, Y.-L., 2010. Radiochimica Acta 98, 577-582.

Schott, J., Kretzschmar, J., Acker, M., Eidner, S., Kumke, M.U., Drobot, B., Barkleit, A., Taut, S., Brendler, V., and Stumpf, T., 2014. Dalton Transactions 43, 11516-11528.

Schott, J., Kretzschmar, J., Tsushima, S., Drobot, B., Acker, M., Barkleit, A., Taut, S., Brendler, V., and Stumpf, T., 2015. Dalton Transactions 44, 11095-11108.

Xiong, Y.-L., Lord, A.C., 2008. Applied Geochemistry 23, 1634-1659.

OBJECTIVE OF THIS STUDY

- To calculate speciation of Am(III) in NaCl solutions in the presence of borate based on the formation constant for $\text{AmHB}_4\text{O}_7^{2+}$ from Xiong (2017), which was evaluated from the raw solubility data from Borkowski et al. (2010).
- To calculate solubility of Am(III) in NaCl solutions in the presence of borate based on the equilibrium constant for $\text{AmB}_9\text{O}_{13}(\text{OH})_4(\text{cr})$ from Xiong (2017), which was evaluated from the raw solubility data from Hinz et al. (2015).
- Modeling platform: EQ3/6 Version 8.0a Wolery et al. (2010) and Xiong (2011).

Borkowski, M., Richmann, M., Reed, D.T., and Xiong, Y.-L., 2010. *Radiochimica Acta* 98, 577-582.

Hinz, K., Altmaier, M., Gaona, X., Rabung, T., Schild, D., Richmann, M., Reed, D.T., Alekseev, E.V. and Geckeis, H., 2015. *New Journal of Chemistry* 39, 849-859.

Wolery, T.J., Xiong, Y.-L., and Long, J., 2010. Verification and Validation Plan/Validation Document for EQ3/6 Version 8.0a for Actinide Chemistry, Document Version 8.10. Carlsbad, NM: Sandia National Laboratories. ERMS 550239.

Xiong, Y.-L., 2011. WIPP Verification and Validation Plan/Validation Document for EQ3/6 Version 8.0a for Actinide Chemistry, Revision 1, Document Version 8.20. Supersedes ERMS 550239. Carlsbad, NM. Sandia National Laboratories. ERMS 555358

Xiong, Y.-L., 2017. *MRS Advances*, in press

The WIPP Borate Model

Table 1. The WIPP borate model for the Na–B(OH)₃–Cl system (from DATA0.FM2, Domski, 2015; Xiong and Domski, 2016) used for evaluation of formation constants for AmHB₄O₇²⁺ and AmB₉O₁₃(OH)₄(cr)

Pitzer Binary Interaction Coefficients					
Species, <i>i</i>	Species, <i>j</i>	$\beta^{(0)}$	$\beta^{(1)}$	C^ϕ	Reference
Na ⁺	B(OH) ₄ ⁻	-0.0427	0.089	0.0114	F & W
Na ⁺	B ₃ O ₃ (OH) ₄ ⁻	-0.056	-0.910		F & W
Na ⁺	B ₄ O ₅ (OH) ₄ ²⁻	-0.11	-0.40		F & W
Pitzer Mixing Parameters and Interaction Parameters Involving Neutral Species					Reference
Species, <i>i</i>	Species, <i>j</i>	Species, <i>k</i>	θ_{ij} or λ_{ij}	Ψ_{ijk} or ζ_{ijk}	F & W
B(OH) ₄ ⁻	Cl ⁻	Na ⁺	-0.065	-0.0073	F & W
B ₃ O ₃ (OH) ₄ ⁻	Cl ⁻	Na ⁺	0.12	-0.024	F & W
B ₄ O ₅ (OH) ₄ ²⁻	Cl ⁻	Na ⁺	0.074	0.026	F & W
B(OH) ₃ (aq)	Cl ⁻		0.091		F & W
B(OH) ₃ (aq)	B ₃ O ₃ (OH) ₄ ⁻		-0.20		F & W
B(OH) ₃ (aq)	Na ⁺		-0.097		F & W
NaB(OH) ₄ (aq)	Na ⁺		0.093		X
Equilibrium Constant for Complex Formation					
Reaction			log K	Reference	
Na ⁺ + B(OH) ₄ ⁻ = NaB(OH) ₄ (aq)			0.25	X	

Domski, P., 2015. Carlsbad, NM: Sandia National Laboratories. ERMS 564914

F & W: Felmy, A.R., and Weare, J.H., 1986. *Geochimica et Cosmochimica Acta*, 50, no. 12, 2771–2783.

X: Xiong, Y.-L., Kirkes, L., and Westfall, T., 2013. *American Mineralogist* 98, 2030–2036.

Xiong, Y.-L., Domski, P., 2016. Carlsbad, NM: Sandia National Laboratories. ERMS 566047.

Equilibrium Constants from Xiong (2017) Consistent with the WIPP Borate Model

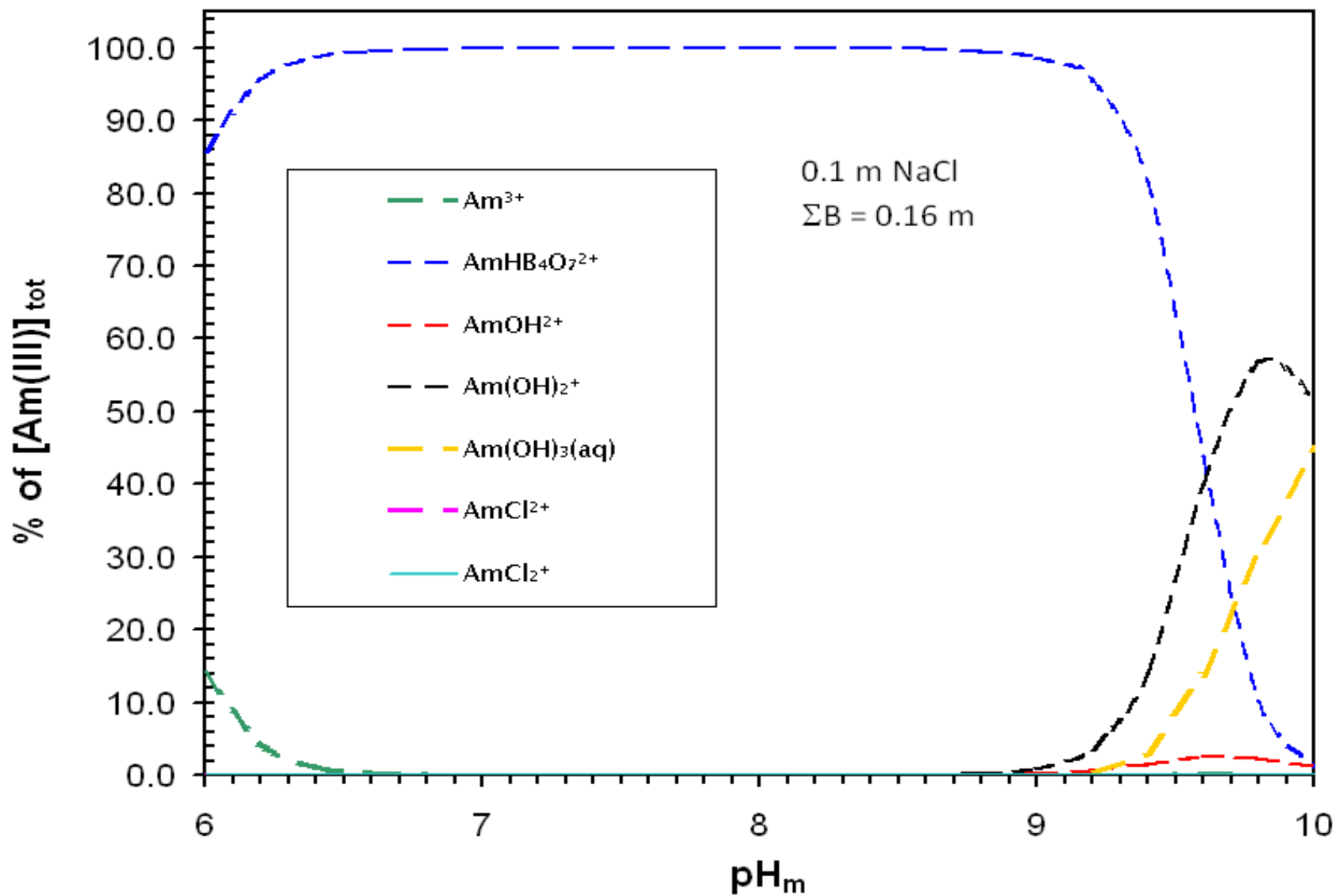
Table 2. Equilibrium constants for $\text{AmHB}_4\text{O}_7^{2+}$ and $\text{AmB}_9\text{O}_{13}(\text{OH})_4(\text{cr})$ at infinite dilution at 25 °C (298.15 K), and associated Pitzer interaction parameters

Reaction		log K at 25 °C		
$4\text{B}(\text{OH})_4^- + 3\text{H}^+ + \text{Am}^{3+} \rightleftharpoons \text{AmHB}_4\text{O}_7^{2+} + 9\text{H}_2\text{O}(\text{l})$		37.34±0.25		
$\text{AmB}_9\text{O}_{13}(\text{OH})_4(\text{cr}) + 19\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Am}^{3+} + 9\text{B}(\text{OH})_4^- + 6\text{H}^+$		-79.30±0.30		
Pitzer Binary Interaction Coefficients				
Species <i>i</i>	Species <i>j</i>	$\beta^{(0)}$	$\beta^{(1)}$	C^ϕ
$\text{AmHB}_4\text{O}_7^{2+}$	Cl^-	0.9163	1.74	0

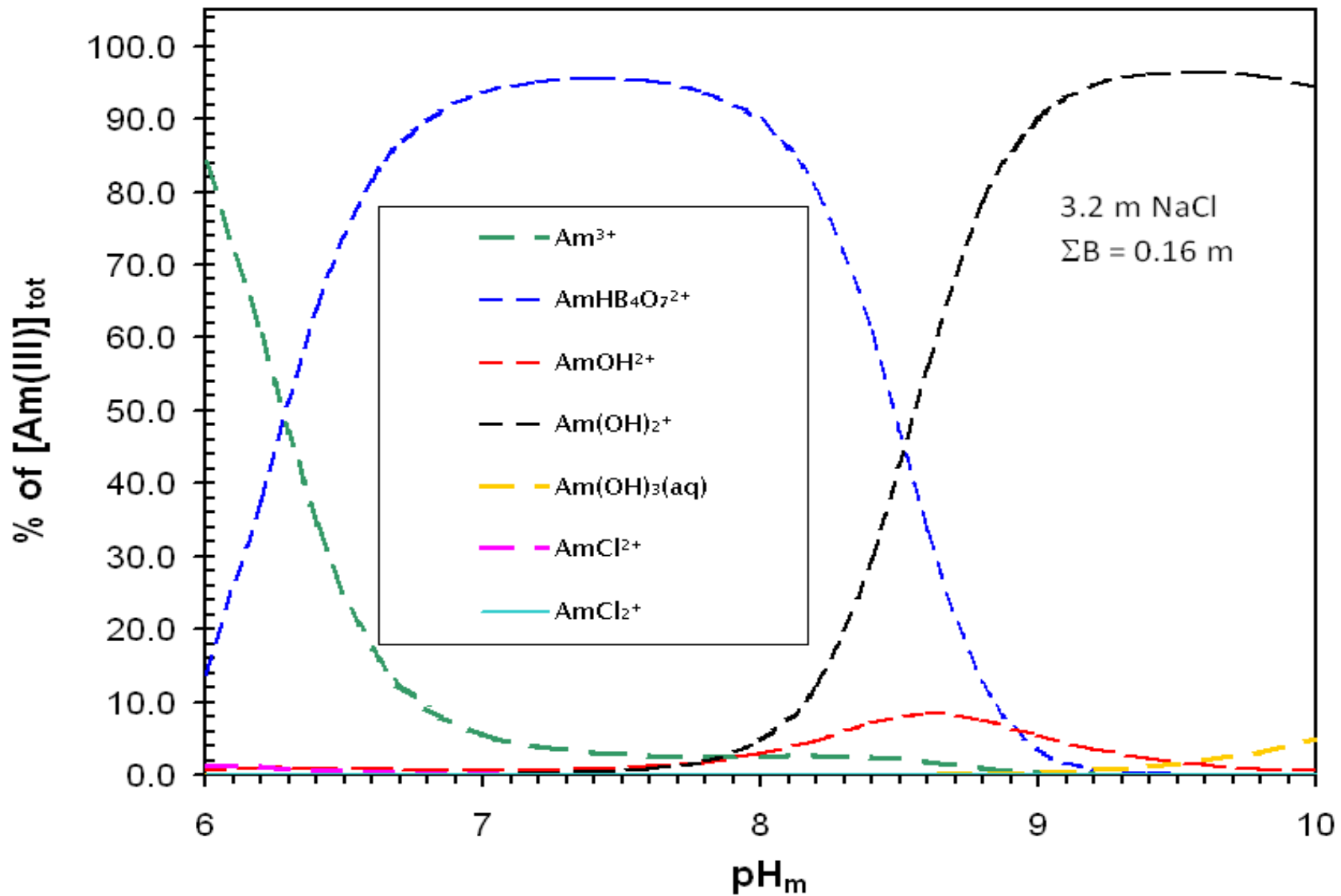
Outline of Speciation Calculations

- Speciation calculations are performed in NaCl solutions ranging from $0.1 \text{ mol} \cdot \text{kg}^{-1}$ to $5.6 \text{ mol} \cdot \text{kg}^{-1}$.
- Speciation calculations are performed at a constant borate concentration of $0.16 \text{ mol} \cdot \text{kg}^{-1}$.
- Am(III) species include Am^{3+} , AmCl^{2+} , AmCl_2^+ , AmOH^{2+} , $\text{Am}(\text{OH})_2^+$, $\text{Am}(\text{OH})_3(\text{aq})$, and $\text{AmHB}_4\text{O}_7^{2+}$.

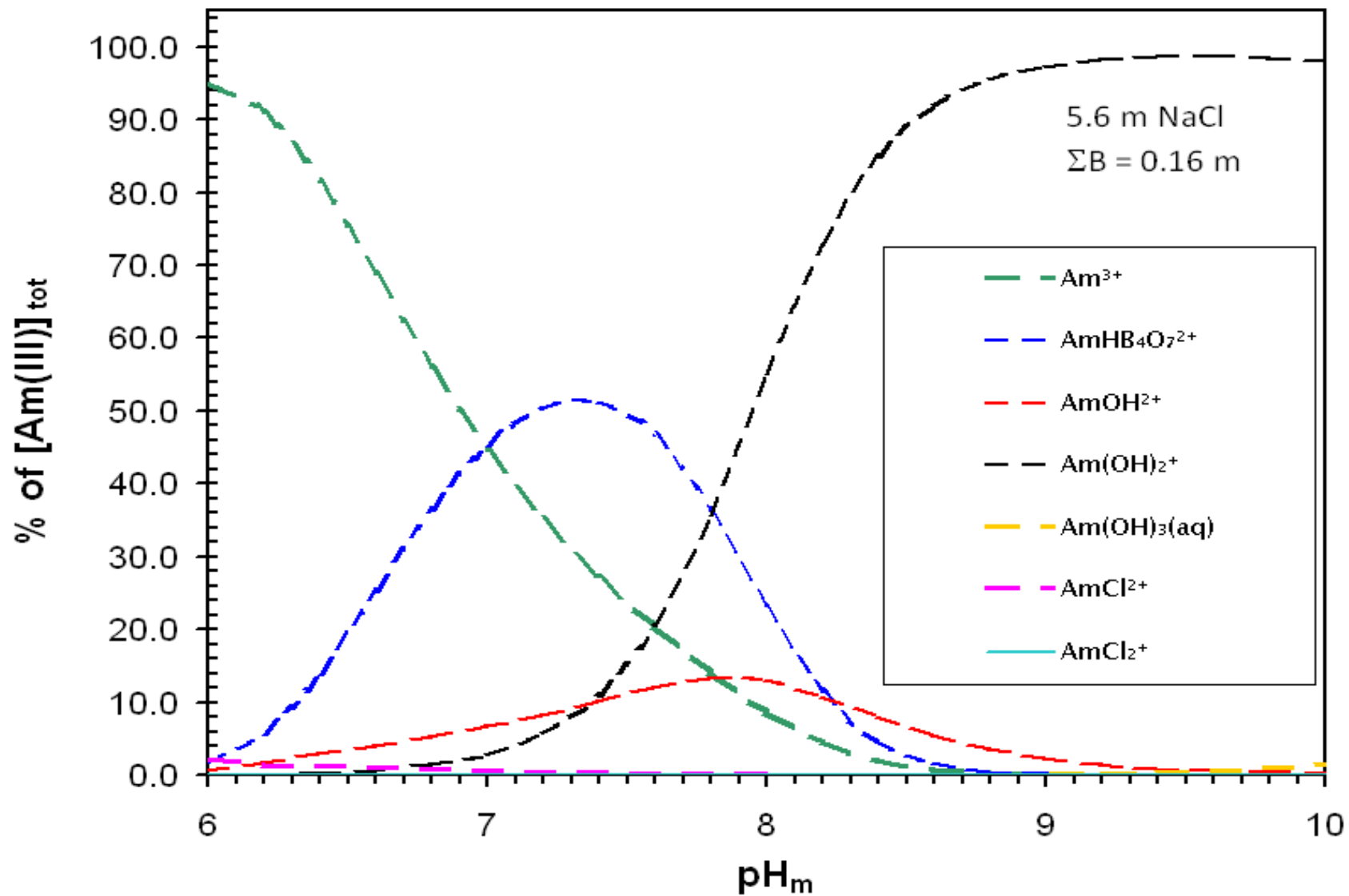
Speciation of Am(III) in NaCl in the Presence of Borate



Speciation of Am(III) in NaCl in the Presence of Borate



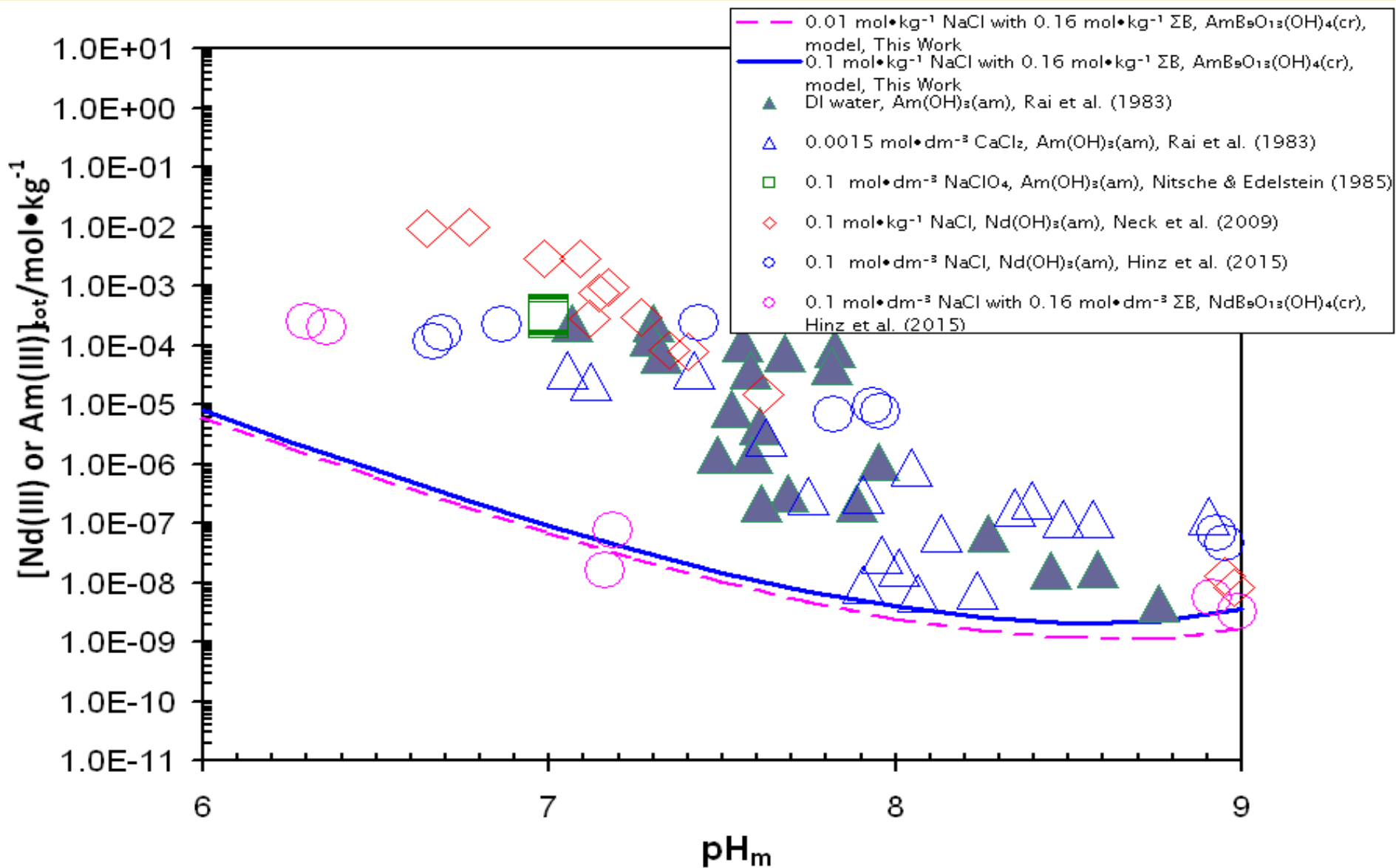
Speciation of Am(III) in NaCl in the Presence of Borate



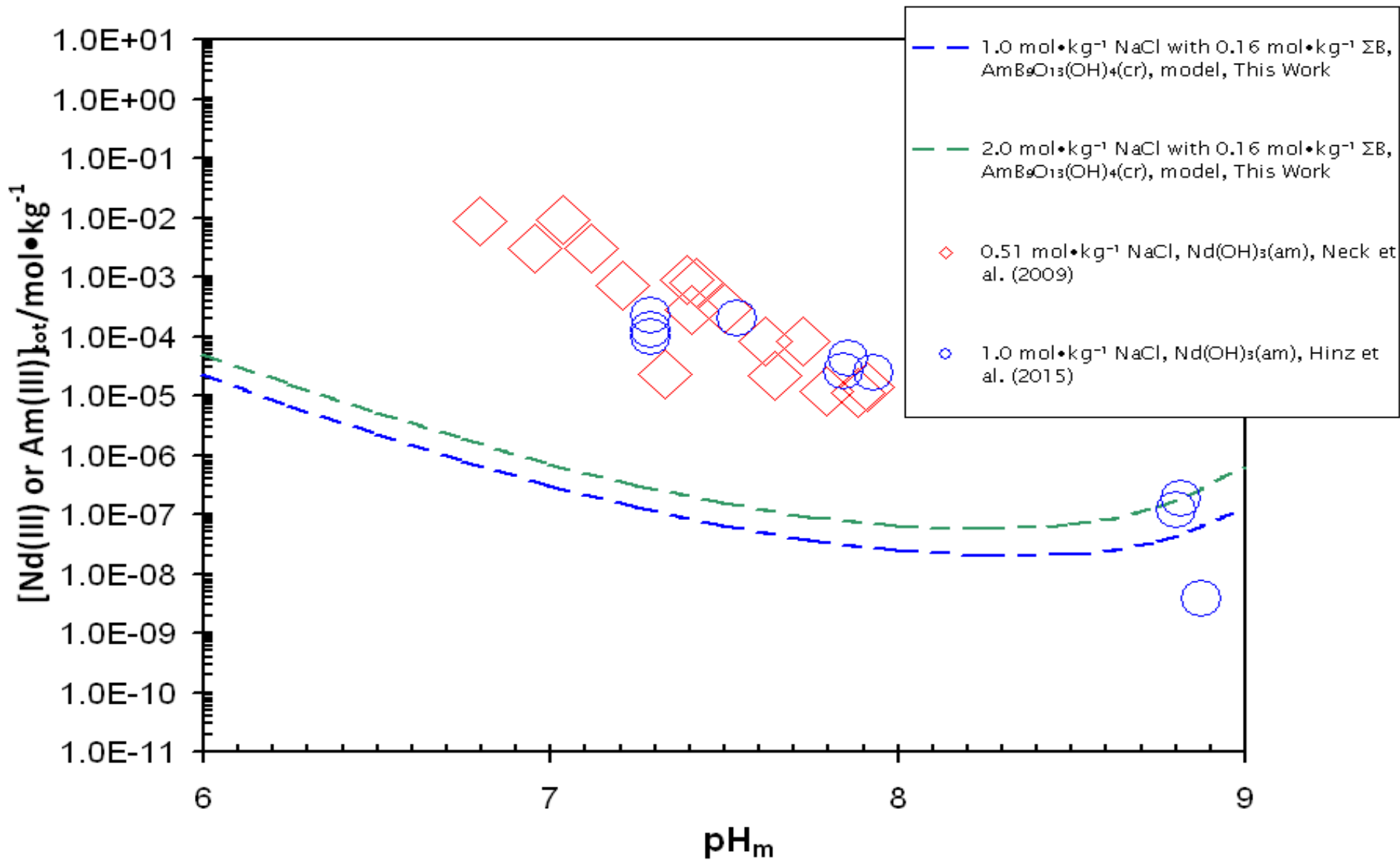
Outline of Solubility Calculations

- Solubility calculations are performed in NaCl solutions ranging from $0.01 \text{ mol}\cdot\text{kg}^{-1}$ to $5.6 \text{ mol}\cdot\text{kg}^{-1}$.
- Solubility calculations are performed at a constant borate concentration of $0.16 \text{ mol}\cdot\text{kg}^{-1}$.
- The solubility-controlling phase is $\text{AmB}_9\text{O}_{13}(\text{OH})_4(\text{cr})$.
- The species contributing to total Am(III) include Am^{3+} , AmCl^{2+} , AmCl_2^+ , AmOH^{2+} , $\text{Am}(\text{OH})_2^+$, $\text{Am}(\text{OH})_3(\text{aq})$, and $\text{AmHB}_4\text{O}_7^{2+}$.
- In addition to experimental data for $\text{NdB}_9\text{O}_{13}(\text{OH})_4(\text{cr})$ from Hinz et al. (2015), experimental data with $\text{Am}(\text{OH})_3(\text{am})$ and $\text{Nd}(\text{OH})_3(\text{am})$ from other sources are also displayed for comparison.

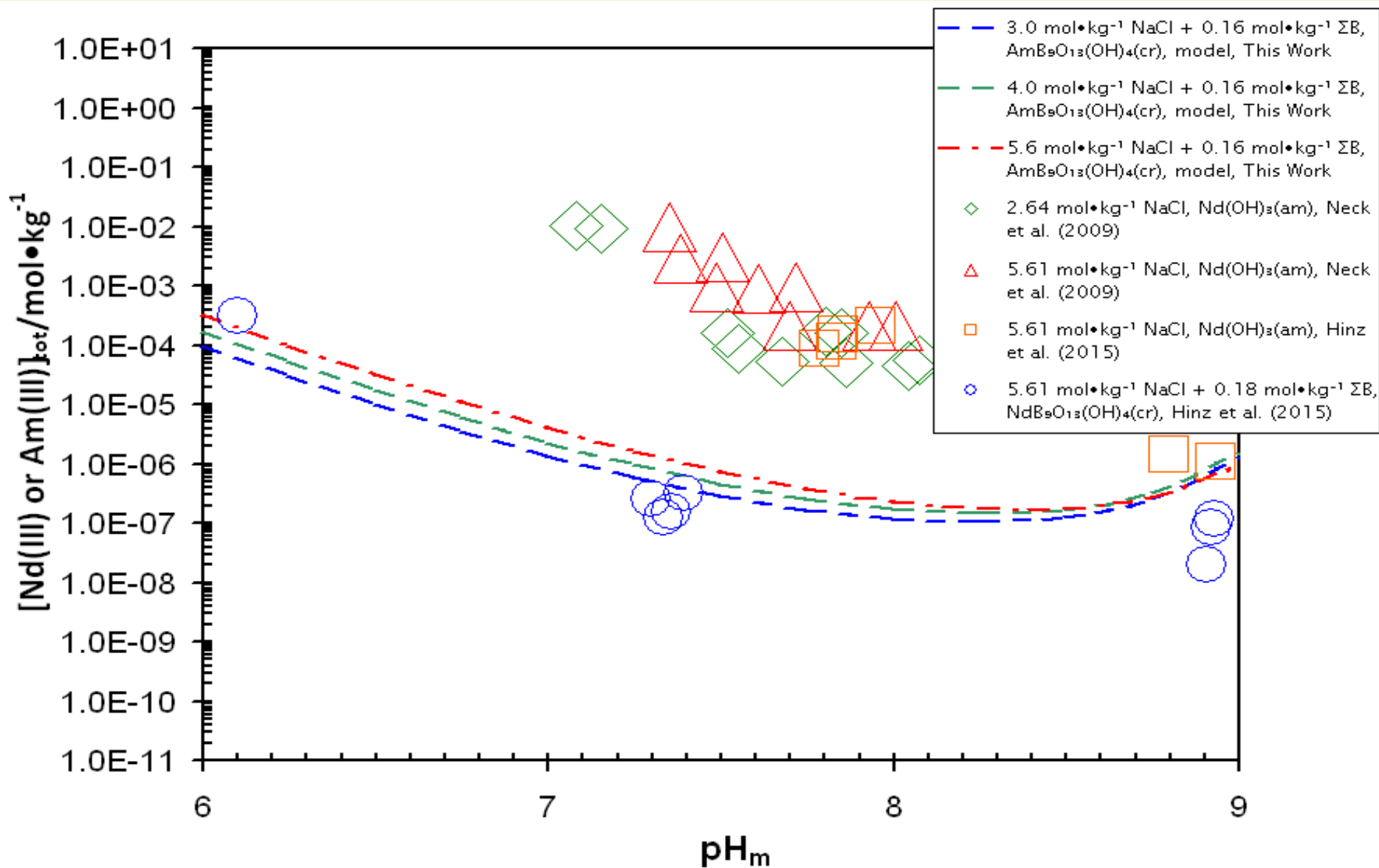
Solubility of Am(III) in NaCl in the Presence of Borate



Solubility of Am(III) in NaCl in the Presence of Borate



Solubility of Am(III) in NaCl in the Presence of Borate



Summary

- Speciation calculations using the formation constant obtained in Xiong (2017) at a constant concentration of borate of $0.16 \text{ mol} \cdot \text{kg}^{-1}$ indicate that:
 - In low concentrations of NaCl such as $0.1 \text{ mol} \cdot \text{kg}^{-1}$, $\text{AmHB}_4\text{O}_7^{2+}/\text{NdHB}_4\text{O}_7^{2+}$ is a dominant species from pH_m 6 to pH_m 9. Above pH_m 9, hydroxyl species dominate.
 - In high concentrations of NaCl such as $3.2 \text{ mol} \cdot \text{kg}^{-1}$, $\text{AmHB}_4\text{O}_7^{2+}/\text{NdHB}_4\text{O}_7^{2+}$ is a dominant species from pH_m 6.4 to pH_m 8.4. Below pH_m 6.4, $\text{Am}^{3+}/\text{Nd}^{3+}$ is a dominant species. Above pH_m 8.4, hydroxyl species dominate.
 - In NaCl concentrations close to saturation of halite $[\text{NaCl}(\text{cr})]$ such as $5.6 \text{ mol} \cdot \text{kg}^{-1}$, the dominant field of $\text{AmHB}_4\text{O}_7^{2+}/\text{NdHB}_4\text{O}_7^{2+}$ is from pH_m 7.0 to pH_m 7.5.

Summary (Continued)

- Solubility calculations using the equilibrium constant for $\text{AmB}_9\text{O}_{13}(\text{OH})_4(\text{cr})$ from Xiong (2017) at a constant concentration of borate of $0.16 \text{ mol} \cdot \text{kg}^{-1}$ indicate that:
 - The solubilities of $\text{AmB}_9\text{O}_{13}(\text{OH})_4(\text{cr})$ are much lower than those for $\text{Am}(\text{OH})_3(\text{am})/\text{Nd}(\text{OH})_3(\text{am})$, in the pH_m region lower than 9;
 - Suggesting that $\text{AmB}_9\text{O}_{13}(\text{OH})_4(\text{cr})$ may be the solubility-controlling phase in solutions in the presence of borate at $\text{pH}_m \leq 9$.